Comparative Study of Mechanical and Morphological Properties of Alumina Coatings Treated by Conventional Furnace and Laser Processing

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***Abstract*— Aluminium oxide coating on metallic substrates has attracted attention for a broad range of applications including wear resistance, oxidation and hot-corrosion resistance, heat and thermal shock resistance and electrical insulation. Alumina coatings were prepared via sol-gel route and then dip-coated on the surface of AISI316 substrates. The alumina-coated substrates were treated by two methods include conventional heat treatment furnace and laser processing to study and compare the phase transition and the mechanical properties of sol-gel alumina coatings. The scanning electron microscope (SEM) and X-ray diffractometer (XRD) were employed to analyse surface morphology and crystalline structure respectively, whilst the mechanical properties were measured using nano-indentation measurements. The results show that the alumina coatings have converted into crystalline aluminium oxide in both phases of γ-Al_2O_3 and α-Al_2O_3. Nano-indentation measurements reveal that the mechanical properties of laser-irradiated alumina coatings in terms of hardness and Young's modulus are much higher than that of the same alumina coatings treated by conventional furnace heating.**

***Keywords*— Alumina coatings; AISI316 substrates; laser processing; furnace heating; Aluminium oxide; Mechanical properties.**

I. INTRODUCTION

THIN films of ceramic coating have been paid a much attention in recent years due to the excellent solutions for the industrial applications against common failures of the surface structure of metallic substrates such as corrosion, oxidation and wear. Synthesis of ceramic thin films via sol-gel method is an effective way due to many advantages such as excellent adhesion to the metal substrates, simplicity, low processing temperature and high purity coatings. Aluminium oxide thin films have been extensively employed in surface modification of metallic substrates due to its chemical inertness, excellent mechanical, optical, and electrical properties, as well as excellent thermal stability [1][2]. The increase of aluminium oxide coating thickness leads to the improvement of the surface properties including corrosion resistance, micro-hardness and electrical properties [3]. Several researchers have been applied sol-gel alumina coatings on the metallic substrates to obtain desired functions such as corrosion and wear properties [4], electrical insulation coatings [5], environmental barrier coatings [6], and high hardness for cutting tools applications [4]. Several applications, hard coatings are required to enhance the surface properties. Generally, the initial sol-gel aluminium oxide coatings are mostly formed in amorphous structure which is soft, hence this amorphous phase need to be crystallised to make it ideal for mechanical applications. The amorphous alumina coatings can be converted into different crystal phases of aluminium oxide including θ-Al_2O_3, γ-Al_2O_3 and α-Al_2O_3 that depends on the calcination conditions, where the α-Al_2O_3 has known as the most stable and hardest structure among them [7,8]. Laser technology is considered as a clean energy source that renders them to be used widely in the surface modification field. The advantage of using laser processing to treat the interface of the coated substrates without affecting the bulk properties of the substrates is desired function that cannot obtained by other techniques such as conventional heat-treatments. Lasers are an effective technology for surface coating with short processing time and are not required sophisticated equipments such as high vacuum and temperature in comparison with physical vapour deposition (PVD), chemical vapour deposition (CVD) and pulsed laser deposition (PLD) [9]. Laser is widely used in surface modification field instead of conventional heat-treatments for the processing of sol-gel coatings, hence, this can be attributed to a wide range of advantages, including low energy consumption, good quality of resulting coatings, short processing time, fast heating/cooling rate, accurate control over the process and an environmentally friendly technology. Laser processing of sol-gel products on the substrates surface have been conducted through versatile ways, including wet sol-gel coating [10], dry sol-gel coating [11] and as nano-particulate powders from sol-gel technology [12]. In this study, we well use the conventional heat-treatment and ytterbium fibre laser technology (wavelength 1064 nm) to produce aluminium oxide coatings on AISI316 substartes to investigate and compare the mechanical properties of the resultant coatings.

II. Experimental

A. Sample Preparation

Alumina sol was synthesised via sol-gel method by using aluminium isopropoxide (98%) as a precursor, isopropanol as a solvent, acetic acid as a catalyst and distilled water as a medium. The reaction system was kept stirring at 80°C for several hours until the system became transparent, indicating that a colloidal alumina dispersion is formed. The AISI316 plates were cut into small pieces approximately 20 × 12 × 2 mm^3 and then carefully prepared by polishing with different grit SiC sand papers and finally 6 µm diamond paste. The chemical composition of AISI316 is listed in Table I.

TABLE I. CHEMICAL COMPOSITION OF THE ASSI316 USED

C (%)	Mn (%)	Si (%)	P (%)	S (%)	Cr (%)	Mo (%)	Ni (%)	N (%)	Fe (%)
0.08	2.0	0.75	0.045	0.03	16.0-18.0	2.0-3.0	10.0-14.0	0.1	balance

B. Characterisation

The X-ray diffraction (XRD), conducted on a Siemens D500 X-ray diffractometer with CuKα radiation at 20 mA and 40 kV, was used to determine the crystalline structure of alumina coatings. Scanning electron micrographs (SEM) was conducted on a Hitachi 3400N SEM to investigate the surface morphology of alumina-coated surfaces. Nano Test^{TM} equipment, supplied by Micro Materials Ltd [13], was used to measure the mechanical properties of alumina-coated surfaces.

III. Results and Discussion

A. X-Ray Diffraction Analysis

The analysis of X-Ray diffraction is shown in Figure 1. The calcining Furnace conditions for alumina coated substrates are summarised in Table II.

TABLE II. THE THERMAL TREATMENT CONDITIONS FOR ALUMINA COATED SAMPLES

Sample	Heating rate (°C/min)	Final temperature (°C)	Holding time (hour)
As-dried alumina substrate	-	-	-
Alumina coated substrate 1	10	850	1
Alumina coated substrate 2	10	1100	1

It is observed that the heat treatment of the alumina coatings dip-coated on the stainless steel substrates at different temperatures using various heating conditions (as shown in Table 2), led to the formation of various alumina structures. The two strong peaks detected at 2θ = 43.6˚ and 50.3˚ belong to the stainless steel substrate [14]. The as-dried alumina coatings at room temperature show no diffraction peaks.The alumina coating transition is clearly seen with the increase of the sintering temperature; therefore, this led to obtain different crystal phases of aluminium oxide, mainly γ-Al_2O_3 and α-Al_2O_3. The coated substrate treated at 850 °C is crystallised in γ-Al_2O_3 form [15]. The coated substrate sintered at 1100 °C is transformed into α-Al_2O_3 phase [16]; however, this sample illustrates the presence of the iron oxide (Fe_2O_3) with α-Al_2O_3 on the stainless steel substrate due to the high temperature required for sintering [17]. This is similar to the behavior of alumina coatings processed by laser technique at various energies, suggesting the conversion of sol-gel alumina coatings into aluminum oxide under the effect of laser irradiation.

Laser irradiation of alumina coatings on stainless steel substrates led to the formation of alumina coatings in different crystalline phases. The laser irradiation conditions for alumina coated substrates illustrate in Table III.

TABLE III. THE LASER ENERGIES DELIVERED TO ALUMINA COATED SAMPLES

Sample	%. of fibres
As-dried alumina substrate	-
Alumina coated substrate 1	10.9 J/mm^2
Alumina coated substrate 2	21.7 J/mm^2

The irradiation of alumina coatings at laser energy density of 10.9 J/mm^2 causes the formation of crystalline alumina coating on the substrate surface in the forms of γ-Al_2O_3 and α-Al_2O_3 [18]. The increase of the laser energy density up to 21.74 J/mm^2 led to the formation of α-Al_2O_3 structure [16], indicating that the laser at this energy density has fully converted the alumina coating into pure aluminium oxide coating without the existence of any other alumina forms.

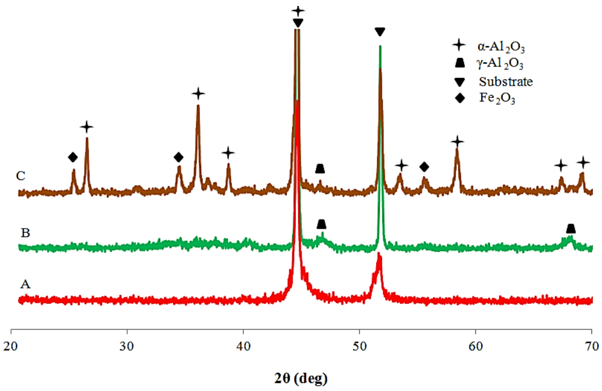

Fig.1. XRD-patterns of the alumina coatings on stainless steel substrates; (A) as-dried coating; (B) heated at 850°C; (C) heated at 1100 °C and laser processed at 10.9 J/mm^2 and 21.7 J/mm^2.

- *Alumina phase transitions*

The various processing conditions of alumina coatings produce different alumina crystalline structures under the effect of heating in both methods including Furnace and laser energy. The obtained alumina crystalline phases are shown in Table IV.

TABLE IV. THE PHASE TRANSITION OF ALUMINA COATINGS UNDER VARIOUS PROCESSING CONDITIONS ACCORDING TO XRD ANALYSIS

Sample	Processing condition	Alumina structure
As-dried alumina coating	-	Amorphous
Alumina coated substrate 1	850 °C	γ-Al_2O_3
Alumina coated substrate 2	1100 °C	α-Al_2O_3
Alumina coated substrate 3	10.9 J/mm^2	α-Al_2O_3
Alumina coated substrate 4	21.7 J/mm^2	α-Al_2O_3

B. *Surface Morphology*

The SEM micrographs show the microstructure and morphology of the alumina coatings on the stainless-steel substrates after heating at different temperatures for 1 hour at 850°C (Fig. 2a), and 1100°C (Fig. 2b), and processed at various laser energies (Fig. 2c, Fig. 2d). It can be clearly seen from (Fig. 1a) and (Fig. 1b) that the substrate surfaces are covered by the alumina coating which consists of many of aluminium oxide particles grown during the high temperature treatment. On the other hand, the surface morphology (Fig 2c, Fig 2d) of the alumina coatings is significantly changed with the increase of the laser deposition energy. The laser-processed alumina coating at energy level of 10.9 J/mm^2 exhibits better uniformity and less roughness over the substrate surface in comparison with that processed at laser energy density of 21.74 J/mm^2. This can be attributed to the low laser energy during the process of the alumina coatings on substrate surface. It is remarkable that surface roughness of the alumina coatings processed by laser technique is higher in comparison with those of conventionally heated alumina coatings.

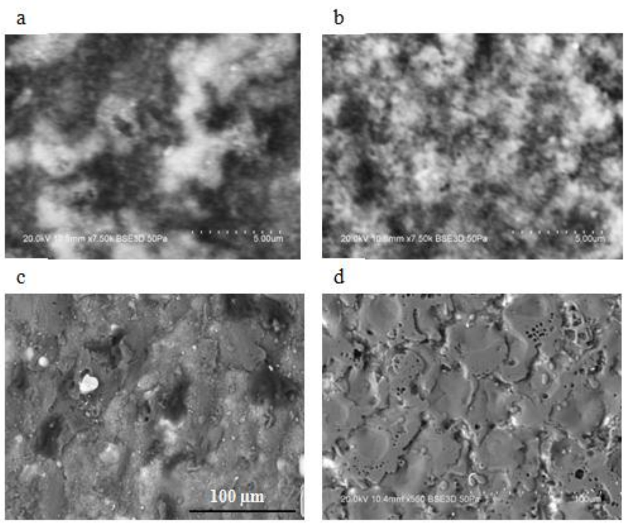

Fig. 2. SEM micrographs of alumina coatings on stainless steel substrates; heated at different temperatures for 1 h, (a) 850°C and (b) 1100°C ; and processed at various laser energies, (c) 10.9 J/mm^2 and (d) 21.7 J/mm^2

C. *Mechanical Properties*

Nano-indentation measurements were performed to examine the mechanical properties of alumina coatings in terms of hardness and Young's modulus.The nano-indentation measurements values of the hardness and Young's modulus of the alumina coatings are presented in Table V.

TABLE V. NANO-INDENTATION MEASUREMENTS FOR ALUMINA COATED SAMPLES

Sample	Processing condition	Values (GPa)
Hardness (GPa)		
As-dried alumina coating	-	0.54
Alumina coated substrate 1	850 °C	2.2
Alumina coated substrate 2	1100 °C	7.2
Alumina coated substrate 3	10.9 J/mm^2	28.4
Alumina coated substrate 4	21.7 J/mm^2	14
Young's modulus (GPa)		
As-dried alumina coating	-	9.7
Alumina coated substrate 1	850 °C	78.3
Alumina coated substrate 2	1100 °C	165.5
Alumina coated substrate 3	10.9 J/mm^2	371.7
Alumina coated substrate 4	21.7 J/mm^2	164

The nano-indentation was conducted with 12 indentations, which were spread in a 3 × 4 array with equal distance of 30 µm from one another for each sample, that is to say an area of 90 × 120 µm is tested. The nano-indentation measurements illustrate a significant improvement of the mechanical properties in terms of hardness and Young's modulus for the alumina coatings after heat treatment and laser processing in comparison with the as-dried alumina coatings at room temperature. The hardness and Young's modulus values as shown in Fig 3, increased for the alumina coatings with the increase of the sintering temperature from 850 °C to 1100 °Cwhich confirms the conversion of the alumina coating into crystal aluminium oxide. Moreover, the improvement of the mechanical properties of the laser-processed alumina coatings can be attributed to the conversion of the amorphous alumina hydrate (as-dried) intoα-form of alumina (α-Al_2O_3) under the influence of the laser energy. These results in good agreement with the XRD analysis, which indicate that the alumina xerogel films have converted into aluminium oxide in different crystal phases. It is clearly seen that the mechanical properties of laser-processed alumina coatings are higher in comparison with those of conventionally heated alumina coatings. Such results indicate that the usage of laser technique at the optimum laser condition can achieve the optimum mechanical properties at the same level as pure α-alumina ceramic, much higher than those of the conventionally heated alumina coatings and the as-dried xerogel alumina.

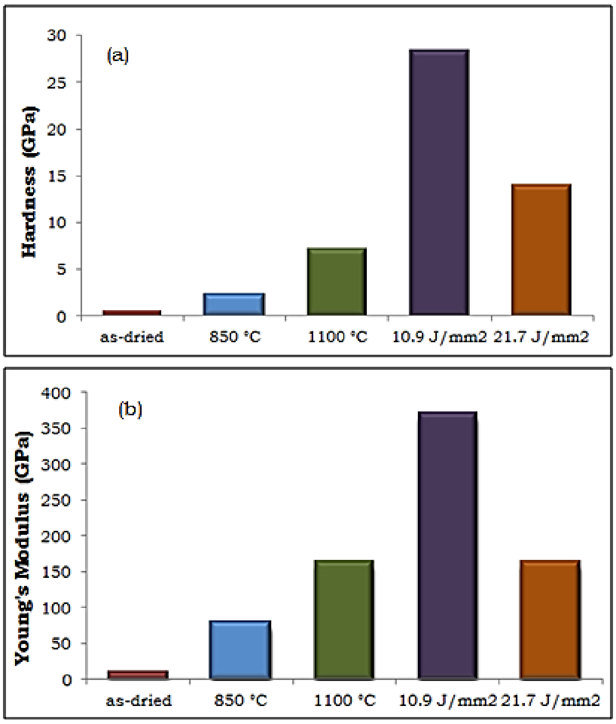

Figure 3. Nano-indentation measurements of conventionally heated alumina coatings and laser-processed alumina coatings: (a) hardness, and (b) Young's modulus.

IV. CONCLUSION

In this paper, alumina coatings have been successfully prepared using sol-gel method. The enhancement of mechanical properties of alumina coatings have been achieved using conventional heat-treatment and laser processing. The SEM micrographs demonstrate that the conventional heat-treatment and laser irradiation leads to the growth of alumina coating particles on the surface of stainless steel substrates. The XRD diffraction patterns prove the conversion of alumina xerogel coating into crystalline aluminium oxide in both phases; γ-Al_2O_3 and α-Al_2O_3 coating. Nano-indentation results reveal that the mechanical properties in terms of hardness and Young's modulus of alumina coatings show a significant improvement after conventional heat-treatment and laser processing in comparison with the as-dried alumina coating. The results also reveal that both techniques are beneficial to obtain hard ceramic alumina coatings with excellent mechanical properties over the surface of metallic substrates. Nano-indentation illustrates that the laser processed alumina coating samples show higher mechanical properties in terms of hardness and Young's modulus, and can reach the optimum mechanical properties of pure α-Al_2O_3, in comparison with the same alumina coating samples heat-treated with conventional Furnace heating.

REFERENCES

[1] C. Jing, X. Zhao, Y. Zhang,Mater. Res. Bull. 42 (2007) 600.

[2] D.C.L. Vasconcelos, R.L. Orefice, W.L. Vasconcelos,Mater. Sci. Eng. 447 (2007) 77.

[3] J.W. Lee, C.W. Won, B.S. Chun, H.Y. Sohn, Mater. Res. 8 (1993) 3151.

[4] G. Ruhi, O.P. Modi, A.S.K. Sinha, I.B. Singh. Corros. sci. 50 (2008) 639.

[5] Y. Ueki, T. Kunugi, N.B. Morley, M.A. Abdou, 85 (2010) 1824.

[6] H. Kim, M. Chen, Q. Yang, T. Troczynski, 420 (2006) 150.

[7] A. Raveh, Z.K. Tsameret, E. Grossman, Surf. Coat. Techn. 88 (1996) 103.

[8] C.H. Hsu, H.P. Teng, F.H. Lu, Surf Coat Techn 205 (2011) 3677.

[9] A.R. Choudhury, T. Ezz, S. Chatterjee, L. Li, Surf. Coat. Techn. 202 (2008) 2817.

[10] T. Ezz, P. Crouse, L. Li, Z. Liu, Surf. Coat. Techn. 200 (2006) 6395.

[11] A.J. López, A. Ureña, J. Rams, Surf. Coat. Techn. 203 (2009) 1474.

[12] M. Masanta, P. Ganesh, R. Kaul, A. R. Choudhury, Surf. Coat. Techn 204(2010) 3471.

[13] H.N. Dhakal, Z.Y. Zhang, M.O.W. Richardson, Polym. Test. 25 (2006) 846–52.

[14] C. Pflitsch, D. Viefhaus, U. Bergmann, B. Atakan, Thin. Solid. Films. 515 (2007) 3653.

[15] S. Kureti, W. Weisweiler, J. Non-Cryst. Solids. 303 (2002) 25.

[16] J. Chandradass, M.H. Kim, D.S Bae, J. Alloys. Compounds. 470 (2009) L9-L12.

[17] B. Wang, R. Yan, D.H. Lee, Y. Zheng, H. Zhao, C. Zheng, J. Analytical.Applied. Pyrolysis 91 (2011) 105-113.

[18] S. Kureti , W. Weisweiler , J. Non-Cryst. Solids.303 (2002) 253–61.